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Ionic Conductivity of Chemically Synthesized $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ Solid Electrolyte

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Abstract. Strontium and magnesium-doped lanthanum gallate is a solid electrolyte with higher ionic conductivity than yttria-stabilized zirconia. This perovskite-type ionic conductor has been investigated for application as solid electrolyte in intermediate-temperature solid oxide fuel cells. In this work the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ composition was synthesized by a soft chemistry route seeking for a more homogeneous microstructure. Densification was carried out by the conventional method and by fast firing. The ionic conductivity of sintered specimens were evaluated by impedance spectroscopy. The apparent density was about 90% and 94% for fast fired and conventionally sintered specimens, respectively. No significant difference was found for the grain conductivity of specimens fast fired at 1500 ºC for 5 min and sintered by the conventional method at 1450 ºC for 4 h.

Introduction

Oxygen-ion conductors based on strontium- and magnesium-doped lanthanum gallate, designated simply by LSGM, have been proposed for application as solid electrolyte in solid oxide fuel cells operating at intermediate temperatures (500-700 ºC), due to their high ionic conductivity and stability over a wide range of oxygen partial pressures [1,2].

The strontium- and magnesium-doped lanthanum gallate compositions have been typically prepared by the conventional mixing of starting oxides followed by solid-state reaction [1,2]. Relatively few reports focused a solution method of synthesis, for which a better chemical homogeneity of the product material is expected [3-7]. Concerning the sintering process, good densification were obtained with microwave [8] and high-pressure spark plasma sintering [9], although most frequently the conventional method of sintering has been used.

In this work, the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) composition was prepared by the cation complexation technique and sintered by the conventional and fast firing methods. The main purpose was to evaluate the effect of the sintering method on the structure and ionic conductivity of the sintered pellets prepared with chemically homogeneous powders.

Experimental

The $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ composition was synthesized by the cation complexation technique as proposed in [10] using high purity precursors. In brief, this method consists in mixing the cation solution to a complexant solution. The mixed solution is heated up to 100 ºC, and after solvent evaporation, the viscosity of the solution increases giving rise to a porous resin. The resin is, then, thermally decomposed and the desired oxide composition is obtained. Cylindrical pellets were prepared by pressing, and sintering experiments were conducted at 1450 ºC for 4 h (conventional method) and 1450 ºC for 5 and 10 min and 1500 ºC for 5 min (fast firing).

Sintered pellets were characterized by X-ray diffraction (Bruker-AXS, D8 Advance) in the 20-80° 2θ range with 0.05° step size, and apparent density measurements by the Archimedes method. Microstructure observations were carried out in a field emission gun scanning electron microscope, FEG-SEM (FEI Inspect F50) after polishing and thermal etching of pellets surface. The ionic conductivity was determined by impedance spectroscopy measurements (HP 4192A) in the 280 - 420 °C and 5 Hz -13 MHz temperature and frequency ranges, respectively. Silver was used as electrode material.

Results and Discussion

The apparent sintered density determined by the immersion method was about 90% and 94% for pellets sintered by fast firing and the conventional method, respectively.

The X-ray diffraction patterns (Fig. 1) of all sintered pellets exhibit only the diffraction peaks (indicated by *) of the orthorhombic structure (*Imma* space group) characteristic of this composition. This result suggests that a single-phase material may be obtained by this method of synthesis, within the experimental error of the characterization technique.

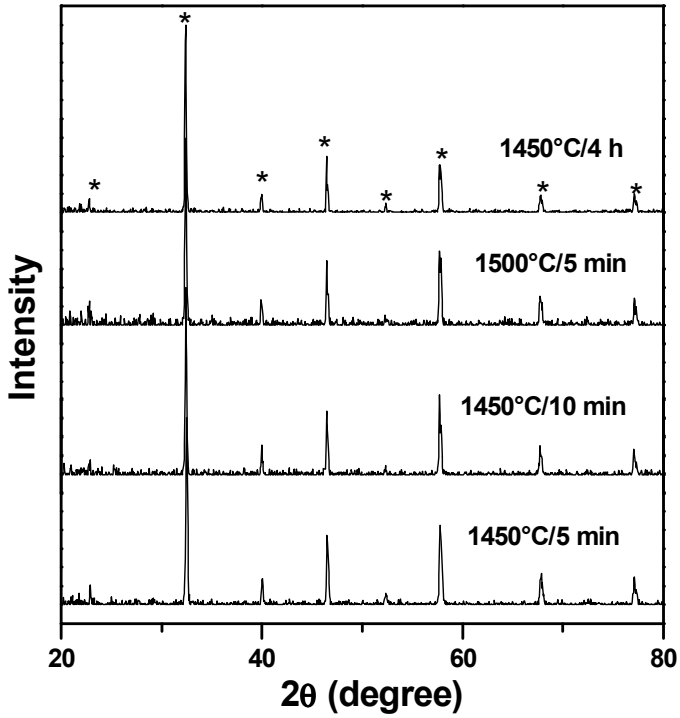
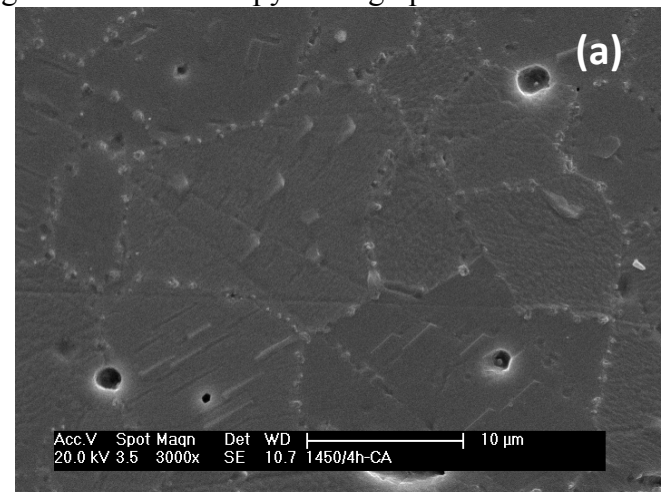


Figure 1 - X-ray diffraction patterns of LSGM pellets sintered by the conventional method and fast firing.

Fig. 2 shows scanning electron microscopy micrographs of LSGM sintered specimens.



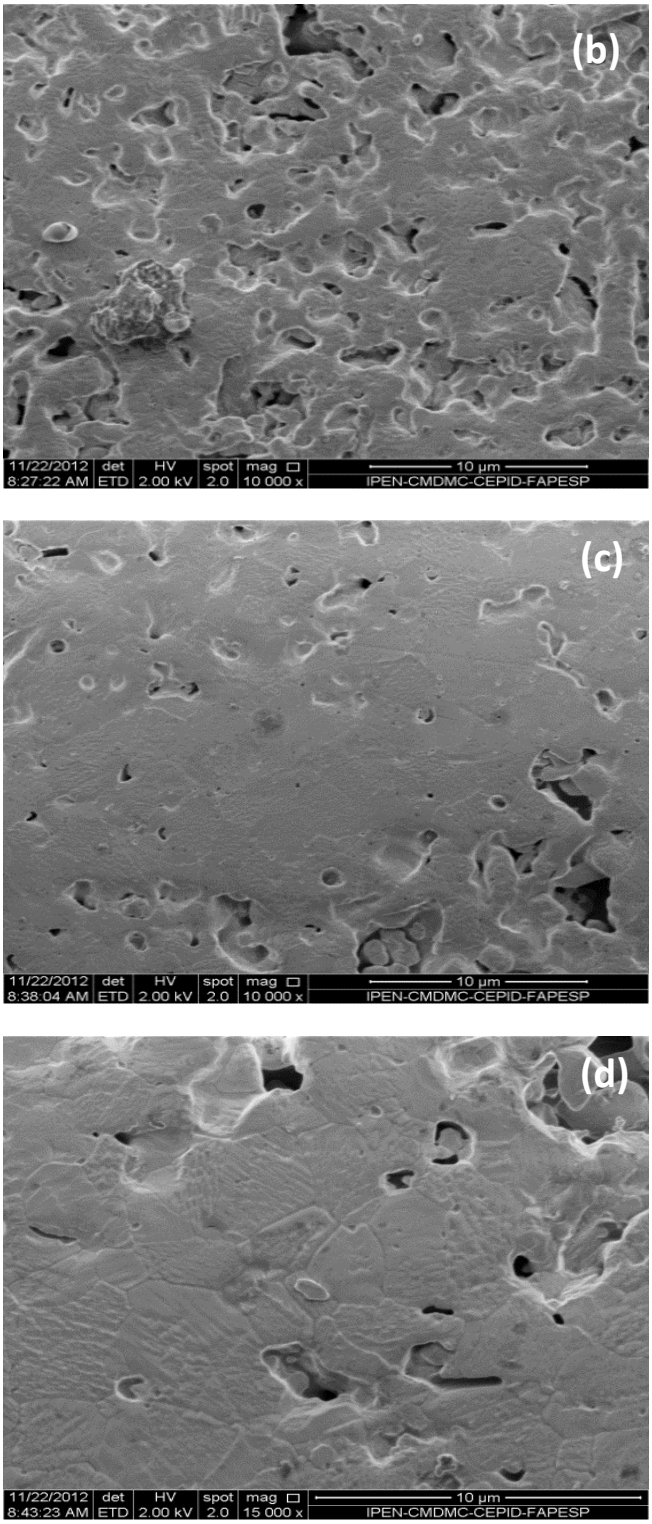


Figure 2 - Scanning electron microscopy micrographs of LSGM sintered specimens: (a) 1450 °C/4 h, (b) 1450 °C/5 min, (c) 1450 °C/10 min and (d) 1500 °C/5 min.

The grain morphology changes considerably depending on the sintering conditions. The FEG-SEM micrograph of the specimen sintered at 1450 °C for 4 h (Fig. 2a) shows intragranular and intergranular porosity, whereas for other specimens the pores are interconnected. For all sintered specimens the main aspects of microstructure, grain size and porosity, are a function of the sintering parameters, i.e., the higher is the sintering temperature or time the smaller is the porosity fraction and the larger is the grain size.

The impedance spectroscopy diagrams at 360 °C (Fig. 3) show two semicircles due to grain and grain boundary resistivities. The numbers over experimental points are the logarithm of the frequency (in Hz). The deconvolution of the whole impedance spectra was not performed due to the overlapping of semicircles, mainly in the intermediate and low frequency ranges. This overlap is primarily attributed to the residual porosity, which constitutes an additional blocking effect to the transport of charge carriers at the grain boundaries [11].

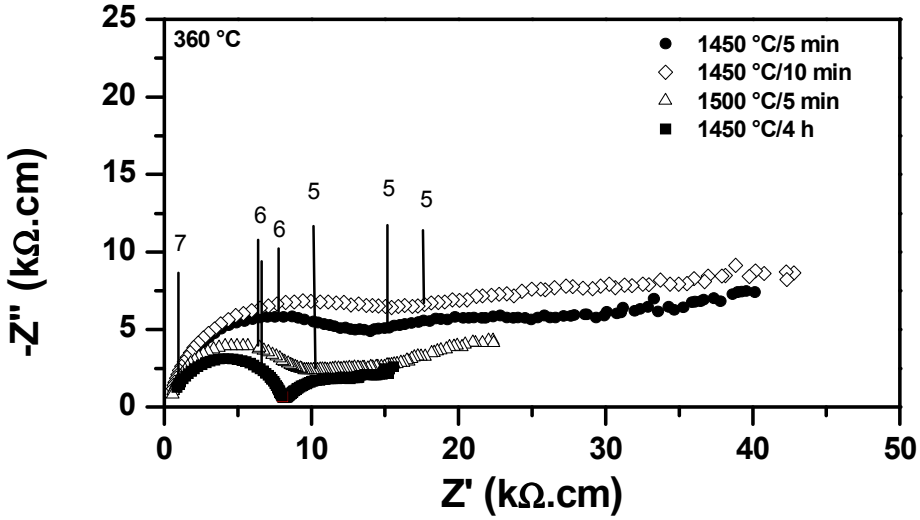


Figure 3 - Impedance spectroscopy diagrams of LSGM sintered specimens.

The pellets sintered at 1500 °C for 5 min exhibit the lowest grain resistivity among those sintered by the fast firing method. This result reveals the role of porosity in this ceramic material.

The temperature dependence of grain conductivity of the sintered pellets is depicted in Fig. 4.

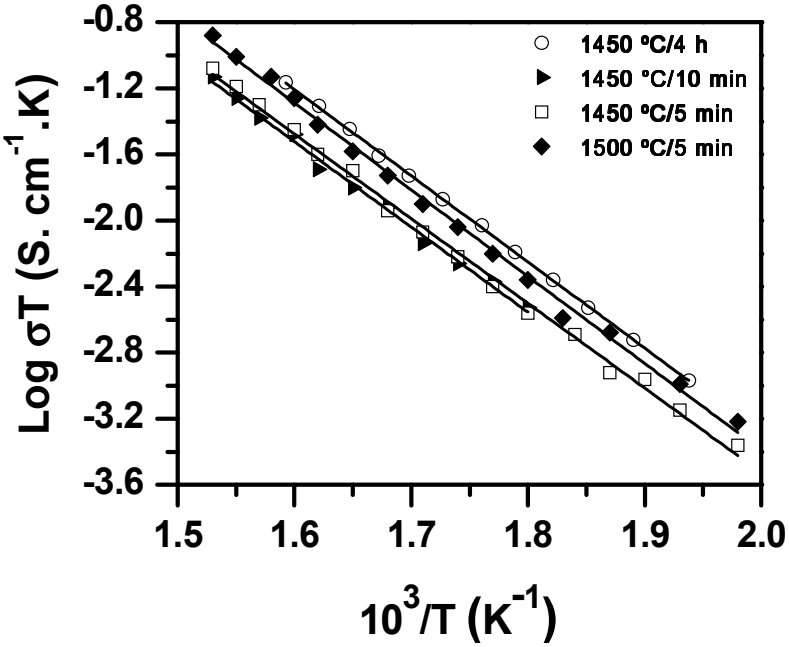


Figure 4 - Arrhenius plots of the grain conductivity of LSGM sintered pellets.

In the restricted range of measuring temperatures, all investigated specimens exhibit similar behavior without change of slope. The straight lines are parallel to each other and the activation energy for grain conduction is about 1.0 eV. High values of grain conductivity were obtained for pellets sintered at 1450 ºC for 4 h and 1500 ºC for 5 min.

Conclusions

LSGM pellets prepared with powders synthesized by the cation complexation technique show relatively high chemical homogeneity, such that no secondary phases were detected by X-ray diffraction. The grain size increases with increasing temperature and time in fast fired specimens. The grain conductivity of fast fired pellets may be adjusted to reach similar values than that of conventionally sintered pellets.

Acknowledgements

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